

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	November 16, 1998	Technical Report # 38	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
Self-Assembled Aggregates of Rod-Coil Block Copolymers and Their Solubilization and Encapsulation of Fullerenes		N00014-94-1-0540 Kenneth J. Wynne R & T Code 3132111	
6. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NUMBER	
Samson A. Jenekhe and X. Linda Chen		# 38	
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)		9. SPONSORING / MONITORING AGENCY NAMES(S) AND ADDRESS(ES)	
University of Rochester Department of Chemical Engineering 206 Gavett hall, Box 270166 Rochester, NY 14627-0166		Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000	
10. SPONSORING / MONITORING AGENCY REPORT NUMBER			
11. SUPPLEMENTARY NOTES Published in Science 279, 1903 (1998).			
12. DISTRIBUTION CODE			
13. ABSTRACT (Maximum 200 words)			
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14. SUBJECT TERMS		15. NUMBER OF PAGES	
Rod-coil diblock copolymers; self-assembly; micelles; solubilization; fullerenes; fullerene encapsulation; fluorescence microscopy.		14	
16. PRICE CODE			
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Standard Form 298 (Rev. 2-89)
Prescribed by ANISE Sad Z39-18
298-102

19981120 164

OFFICE OF NAVAL RESEARCH

GRANT NO: N00014-94-1-0540

R&T Code 3132111
Kenneth J. Wynne

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Prepared for Publication

In

Science, vol **279**, 1903 (1998)

Department of Chemical Engineering
University of Rochester, New York 14627

November 16, 1998

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Self-Assembled Aggregates of Rod-Coil Block Copolymers and Their Solubilization and Encapsulation of Fullerenes

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Amphiphilic poly(phenylquinoline)-*block*-polystyrene rod-coil diblock copolymers have been observed to self-organize into robust, micrometer-scale, spherical, vesicular, cylindrical, and lamellar aggregates from solution. These diverse aggregate morphologies were observed at each composition but their size scale decreased with decreasing fraction of the rigid-rod block. Compared to coil-coil block copolymer micelles, the present aggregates are larger by about two orders of magnitude and have aggregation numbers of over 10^8 . The spherical and cylindrical aggregates have large hollow cavities. Only spherical aggregates with aggregation numbers in excess of 10^9 were formed in the presence of fullerenes (C_{60} , C_{70}) in solution, resulting in the solubilization and encapsulation of over 10^{10} fullerene molecules per aggregate.

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Block copolymers can produce numerous phase-separated microstructures and nanostructures that are of wide scientific and technological interest (1-12). Conventional applications of such block copolymer assemblies include thermoplastic elastomers, pressure-sensitive adhesives, colloidal dispersants, compatibilizers of polymer blends, foams, and surface modification (2-4, 6-8). Of the factors that determine the microstructure of block copolymers, conformational asymmetry between the blocks is perhaps the least understood (5, 11). Theoretical studies of rigid-rod-flexible coil block copolymers, in which the ultimate conformational asymmetry is achieved, have predicted major differences in phase behavior, self-assembly, and microstructures compared to flexible coil-coil block copolymers (11). However, only few experimental studies of synthetic rod-coil block copolymers have been reported (5).

We describe the self-assembly from solution, micelle-like aggregate morphologies, aggregate supramolecular structure, and solubilization properties of a synthetic rod-coil diblock copolymer, poly(phenylquinoline)-*block*-polystyrene (PPQ-*b*-PS) (Fig. 1). The heterocyclic rigid-rod polyquinoline block allows tuning of its amphiphilicity. For example, through protonation or quaternization of the imine nitrogen (13), the rodlike block can be turned into a polyelectrolyte. The π -conjugated nature of the rigid-rod block confers electroactive and photoactive properties (13, 14) on the block copolymers while providing novel ways of probing the self-assembly, molecular packing, morphology, and dynamics of the polymeric amphiphiles by optical and photoelectronic techniques. The amide linkage at the rod-coil interface in each block copolymer chain provides a means of strong intermolecular interactions, through hydrogen bonding, that might enhance the stability of self-organized structures. The PPQ-PS copolymers, in selective solvents for PPQ form large aggregates with various morphologies (spheres, vesicles, cylinders, and lamellae) that can be observed by optical microscopy (OM). Surprisingly, spherical fullerenes (C_{60} , C_{70}) can be solubilized to a large degree by solutions of the rod-coil block copolymers, resulting in the encapsulation of huge numbers ($\sim 10^{10}$) of fullerene molecules.

The synthesis, purification, and characterization of PPQ₅₀-PS₃₀₀ and PPQ₁₀-PS₃₀₀ (subscripts are monomers per block) are described elsewhere (15). Dilute solutions (0.5 to 1.0 mg/ml) of each diblock copolymer in mixed solvents, trifluoroacetic acid (TFA): dichloromethane (DCM) or TFA: toluene at various volume ratios, were used for aggregation studies. Because TFA is a good solvent for PPQ block and protonates its imine nitrogens, whereas the PS block is insoluble in it, micelle-like aggregates (Fig. 1) result from manipulating the solvent composition. The expected structure of such an aggregate in the TFA solution is an inner PS block surrounded by the protonated PPQ shell. This basic aggregate structure is expected to be retained in the solid state after solvent evaporation, which also deprotonates the PPQ block (Fig. 1). The self-assembly of a rod-coil diblock copolymer in a selective solvent for the rigid-rod block has not been theoretically investigated (11) but is experimentally accessible here because of the differential solubility of PPQ and PS blocks. Self-assembly of discrete aggregates of the rod-coil diblock copolymers did not occur from solutions in non-selective solvents, such as nitromethane containing GaCl₃ (15).

Four different, micelle-like aggregate morphologies were observed in PPQ₅₀-PS₃₀₀ by OM and scanning electron microscopy (SEM): spheres, lamellae, cylinders, and vesicles (Fig. 2). The main factors determining morphology were the initial solvent composition (TFA:DCM ratio) and the solution drying rate. Spherical aggregates with a wide distribution of sizes, typically 0.5 to 10 μ m diameters, were observed by rapid drying of solutions on a heated substrate at 95°C. Aggregates prepared by drying solutions at room temperature had

nonspherical morphologies, and each sample was predominantly (~70%) either lamellae, cylinders, or vesicles depending on the initial solvent composition; the minor phases in these morphologies were cylinders, lamellae, or spheres, respectively. Lamellar aggregates have diameters in the 5 to 30 μm range, the cylinders are relatively uniform in diameter (1 to 3 μm) but highly polydisperse in length (5 to 25 μm), and vesicles have outer diameters of about 0.5 to 1.0 μm and wall thickness of about 200 nm. Similar multiple morphologies were observed in aggregates of $\text{PPQ}_{10}\text{-PS}_{300}$, whose average sizes were all smaller than those of $\text{PPQ}_{50}\text{-PS}_{300}$ by about a factor of 2. Repeated heating of the aggregates to 200°C, which is above the glass transition (T_g) of PS blocks ($T_g = 100^\circ\text{C}$) and below that of PPQ blocks ($T_g > 350^\circ\text{C}$) (13), did not have any effect on the aggregate morphologies, which demonstrates the robustness of these aggregates. Also, the polydispersity of the rigid-rod block (15) apparently has no discernible effect on the aggregate morphologies. Compared to recently observed multiple morphologies in coil-coil block copolymers (12), the present aggregates are larger by about two orders of magnitude.

The unusually large sizes of the spherical and cylindrical aggregates, unlike bilayer vesicles and lamellae that could in principle grow to any size, cannot be explained by a simple core-shell structure of conventional block copolymer micelles (3, 6-8, 11-12). The main difficulty is that the rod-coil block copolymer chains from which the aggregates are assembled have on average fully extended lengths of at most ~100 nm (16). Spherical and cylindrical aggregates of about 200 nm diameter are thus expected if solid PS-core/PPQ-shell assemblies were formed. In contrast, the observed aggregates are about 10 to 50 times larger (Fig. 2). To account for the size difference we propose that the observed spherical and cylindrical aggregates form large hollow cavities. An aggregate structure in accord with this hypothesis is cavity-core/PS-inner shell/PPQ-outer shell (Fig. 1). For a typical 5- μm diameter spherical aggregate, 89% of its total volume of $65 \mu\text{m}^3$ is empty. The driving force for the large size and hollow cavity of these aggregates appears to be a more efficient packing of the rigid-rod blocks and, consequently, a more ordered and stable aggregate structure. All the different aggregates under cross-polarizers showed that they were highly ordered with crystalline features. The aggregation number, N_o , or number of diblock copolymer chains per aggregate, was estimated to be 1×10^8 and 3×10^8 for the spherical and cylindrical aggregates, respectively (17).

Aggregate luminescence of $\text{PPQ}_{50}\text{-PS}_{300}$ was explored as a means of probing the molecular packing of the luminescent rigid-rod PPQ blocks in the different aggregate morphologies. Different photoluminescence (PL) emission and excitation spectra were observed for spherical, lamellar, and cylindrical aggregates (Fig. 3). A blue emission band with peak at 454 nm for the spherical aggregates can be interpreted as coming from PPQ blocks that are not parallel. In contrast, both lamellar and cylindrical aggregates have broad emission bands with peaks at 576 and 594 nm, respectively, which are close to the PL emission band ($\lambda_{\text{max}} = 578 \text{ nm}$) of the similarly excited PPQ homopolymer thin film (18). The similarity of the emission spectra of the lamellar and cylindrical aggregates to that of the homopolymer, which is known to luminesce through excimer-like aggregates (18, 19) suggests a high degree of close packing of PPQ block chains in the lamellar and cylindrical aggregates. The different molecular packing of PPQ blocks in the spherical and lamellar and cylindrical aggregates is confirmed by the PL excitation spectra monitored at the respective emission peaks (Fig. 3). Whereas the spherical aggregates show an absorption peak at 390 nm, which is similar to the absorption spectrum of the PPQ homopolymer, the lamellar and cylindrical aggregates have two absorption peaks (406 and 423 nm) and a shoulder (~460 nm) in their excitation spectra. Time-resolved PL decay

dynamics of the fluorescent PPQ block in the different aggregate morphologies evidenced different excited-state lifetimes (Fig. 3). Compared to the PPQ homopolymer thin film, which exhibits two lifetimes (1.1 and 4.7 ns), the PL decay dynamics of PPQ blocks in the spherical aggregates is approximately described by a single lifetime of 0.93 ns. However, in the lamellar and cylindrical aggregates, biexponential lifetimes of 0.38 and 3.5 ns and 0.34 and 2.6 ns, respectively, best fit the decay dynamics. These results suggest that the observed morphology-dependent emission properties of the block copolymer aggregates reflect the varying molecular packing of the fluorescent rigid-rod block.

Fluorescence photomicrographs (Fig. 4) confirmed the aggregate sizes and shapes observed in OM and SEM and revealed that the fluorescent rigid-rod blocks are located at the outer shells of the aggregates, as depicted in the model of Fig. 1. The hollow microcavity and closed ends of the cylindrical aggregates were also revealed (Fig. 4C). The entire ~200nm bilayer thickness of each vesicle appears to fluoresce because the ~140-nm separation between the PPQ blocks in the bilayers is below the resolution limit (Fig. 4D). Also, because of three-dimensional (3D) symmetry and uniformity of emission, the microcavity of the spherical aggregates could not be directly observed (Fig. 4A) but can be inferred from that of similarly formed cylinders (Fig. 1). The 3-D nature of the spherical aggregates can be clearly distinguished from the relatively flat (2D) lamellae, which have rough surfaces.

The large sizes, aggregation numbers, and microcavities of these micelle-like aggregates suggest that the block copolymer assemblies in solution might be capable of solubilization of large molecules or the encapsulation of nanoparticles. We studied the solubilization of the fullerenes C₆₀ and C₇₀ because of their large sizes, generally poor solubility (20-22), and the prospect of preparing block copolymer aggregates with encapsulated fullerenes. Although some guest-host complexes of C₆₀ with γ -cyclodextrin (23), calixarenes (24), and hydroquinone (25) have been reported, few host molecules have large enough cavities to be able to encase one molecule of C₆₀ or the higher fullerenes (20, 26). Although C₆₀ is slightly soluble in pure DCM (0.254 mg/ml, 0.192 mg/g) and pure toluene (2.8 mg/ml, 3.16 mg/g) at 22 to 30°C (20-22), both C₆₀ and C₇₀ were insoluble in pure TFA, TFA/DCM, or TFA/toluene(1:1, v/v). However, both fullerenes were soluble in the mixed solvents containing PPQ₅₀-PS₃₀₀ or PPQ₁₀-PS₃₀₀ diblock copolymer at 25°C, demonstrating the solubilization of C₆₀ and C₇₀ in the block copolymer aggregates. These spherical aggregates with solubilized fullerenes (5 wt %) from TFA/DCM (Fig. 5A) and TFA/toluene (Fig. 5B) have typical diameters in the 15 to 30 μ m range which are about a factor of 3 larger than those of the average pure block copolymer aggregates. The size of the spherical aggregates increased as the amount of fullerene incorporated increased from 1 to the solubility limit of 6 wt %. The corresponding solubilization capacities at 5 and 6 wt % are 3 and 3.7 fullerene molecules per diblock chain, respectively. At 7 to 10 wt % fullerene (C₆₀ or C₇₀) or higher, OM observations showed the coexistence of the discrete spherical aggregates with additional needle-like and continuous fullerene phases. Our proposed structure of the spherical rod-coil block copolymer aggregates with encapsulated fullerenes (Fig. 5C) assumes that the microcavity as well as the inner shell of PS blocks are partially filled with fullerene molecules, whereas the rigid-rod PPQ outer shell blocks are free of fullerenes. Exclusion of fullerene from the rigid-rod shell is reasonable because of the available microcavity, compatibility with PS, and the difficulty of packing spherical molecules with the rodlike blocks. OM observation of aggregates containing fullerenes under cross-polarizers evidenced a highly ordered and crystalline structure (Fig. 5B). We have estimated N_o for aggregates containing 5 and 6 wt % C₆₀ to be of order 6×10^9 and 2×10^{10} , respectively (17). N_o significantly increased upon

solubilization of the fullerenes. These aggregation numbers combined with the observed solubilization capacities of fullerene molecules per diblock chain at 5 and 6 wt %, respectively, mean that $> 10^{10}$ fullerene molecules are encapsulated in each block copolymer aggregate of Fig. 5.

The observed 64 mg of solubilized fullerene (C_{60} or C_{70}) per gram of diblock copolymer represents a solubility enhancement by factors of 330 and 20 compared to pure DCM and toluene, respectively. The best previously reported C_{60} solubility in a solvent is for 1-chloronaphthalene at 42.7 mg/g (21,22). The observed large solubilization capacity of the block copolymer assemblies for the fullerenes can be partly understood in terms of thermodynamic theory of solubilization (9). The similarity of the solubility parameters of fullerene- C_{60} (δ_f) and polystyrene (δ_{ps}) at 25°C is expected to give a very small value of the Flory-Huggins interaction parameter $\chi_{f,ps}$ expressed in terms of the solubility parameters (9). From the reported $\delta_f = 10$ for C_{60} at 25°C (20) and $\delta_{ps} = 8.7$ to 9.9 (9), $\chi_{f,ps} = (\delta_f - \delta_{ps})^2 v_f / k_B T \sim 0.015$, where v_f is molar volume, k_B is the Boltzmann's constant, and $T = 298K$. Correlation of C_{60} solubility to the solubility parameter of many solvents has shown that the largest solubility was observed in solvents with solubility parameters close to that of C_{60} (20, 21). However, one of the most remarkable effects of the introduction of C_{60} or C_{70} into the amphiphilic block copolymer solution is the preferential self-assembly of spherical aggregates. The presence of these essentially spherical fullerene molecules inhibits the self-assembly of nonspherical aggregates of the block copolymers, suggesting that a type of spherical guest-host recognition (26) may also be at play in the solubilization and encapsulation of fullerenes in the block copolymers aggregates.

These results demonstrate the macromolecular self-assembly of stable, well-defined aggregates with size scale in the tens of micrometers and molecular weights of up to 10^{13} daltons, which are among the largest known self-assembled nonbiological structures (27). Possible applications for these rod-coil block copolymer assemblies including microencapsulation, catalyst support, low dielectric constant materials for electronic packaging, and light weight composites derive from their sizes and large microcavities (28). As tunable microcontainers and solubilizers of fullerenes, amphiphilic block copolymers hold potential for the preparation of clusters of and the large-scale extraction, purification, and processing of fullerenes (20). Their combination of electroactive/photoactive properties with self-assembly, robustness, and discrete micrometer-scale particles suggests electrophotographic imaging (29) and other optoelectronic applications (14).

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15. For details on the synthesis, characterization, and aggregation experiments on PPQ-b-PS block copolymers, see the Supplementary Material. For details on our photoluminescence experimental techniques, see: J. A. Osaheni and S. A. Jenekhe, *J. Am. Chem. Soc.* **117**, 7389 (1995).
16. From x-ray diffraction data on oligoquinolines (A. S. Shetty, et al., *Chem. Mater.* submitted) the repeat unit length of PPQ is 0.64 nm. We estimate the repeat unit length of extended chain PS to be ~0.226 nm. Therefore the maximum extended chain lengths of PPQ₅₀-PS₃₀₀ and PPQ₁₀-PS₃₀₀ will be ~100 and ~74 nm, respectively.

17. Order of magnitude of the aggregation number N_o was estimated as follows. About 2×10^5 discrete spherical aggregates/mm² was measured from a photomicrograph taken from a 1 mg diblock copolymer sample covering a total area of 5 cm². Thus, one gets 2.4×10^{-16} mole diblock/aggregate (or 10^{-8} mg diblock/aggregate) or $N_o = 1.5 \times 10^8$. For a typical 5- μm diameter spherical aggregate with 65 μm^3 volume which is 89% empty, assuming an aggregate density of 0.2g/cm³ gives an N_o of 2×10^8 in agreement with the direct experimental estimate. Similar procedures for cylindrical aggregates gave 2×10^4 aggregates/mm² from a photomicrograph taken on a 0.2 mg diblock copolymer sample covering a 5 cm² area. From this, one gets 4.8×10^{-15} mole diblock/aggregate or $N_o = 3 \times 10^8$. In the case of PPQ₅₀-PS₃₀₀ aggregates containing 5 wt % solubilized C₆₀, 10³ spherical aggregates/mm² was measured from a photomicrograph taken from a 0.2 mg diblock/C₆₀ sample covering a 5 cm² area. From this information one gets 9.6×10^{-15} mole diblock/aggregate or $N_o = 6 \times 10^9$. Similarly, for the case of aggregates containing 6 wt % C₆₀, $N_o = 2 \times 10^{10}$.
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30. We thank Ashok S. Shetty for helpful discussion and technical assistance. This research was supported by the Office of Naval Research and in part by the National Science Foundation (CTS-9311741, CHE-9120001).

FIGURE CAPTIONS

Fig. 1. Chemical structure and schematic illustration of the self-assembly of PPQ-b-PS rod-coil diblock copolymers into hollow aggregates.

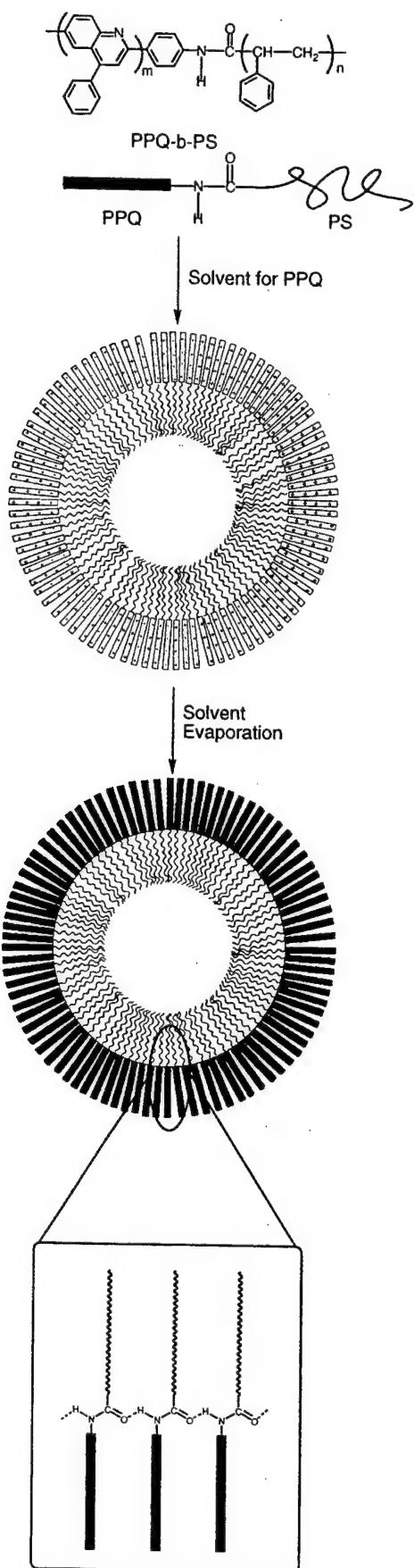
Fig. 2. Optical (A to C) and scanning electron (D) micrographs of the typical morphologies of PPQ₅₀-PS₃₀₀. Drops of dilute solutions (0.5 to 1.0 mg/ml) of the diblock copolymers were spread and dried on glass slides and aluminum substrates, respectively. (A) spherical aggregates (1:1 TFA:DCM, v/v, 95°C); (B) lamellae (1:1 TFA:DCM, 25°C); (C) cylinders (9:1 TFA:DCM, 25°C); (D) vesicles (1:1 – 1:4 TFA:DCM, 25°C).

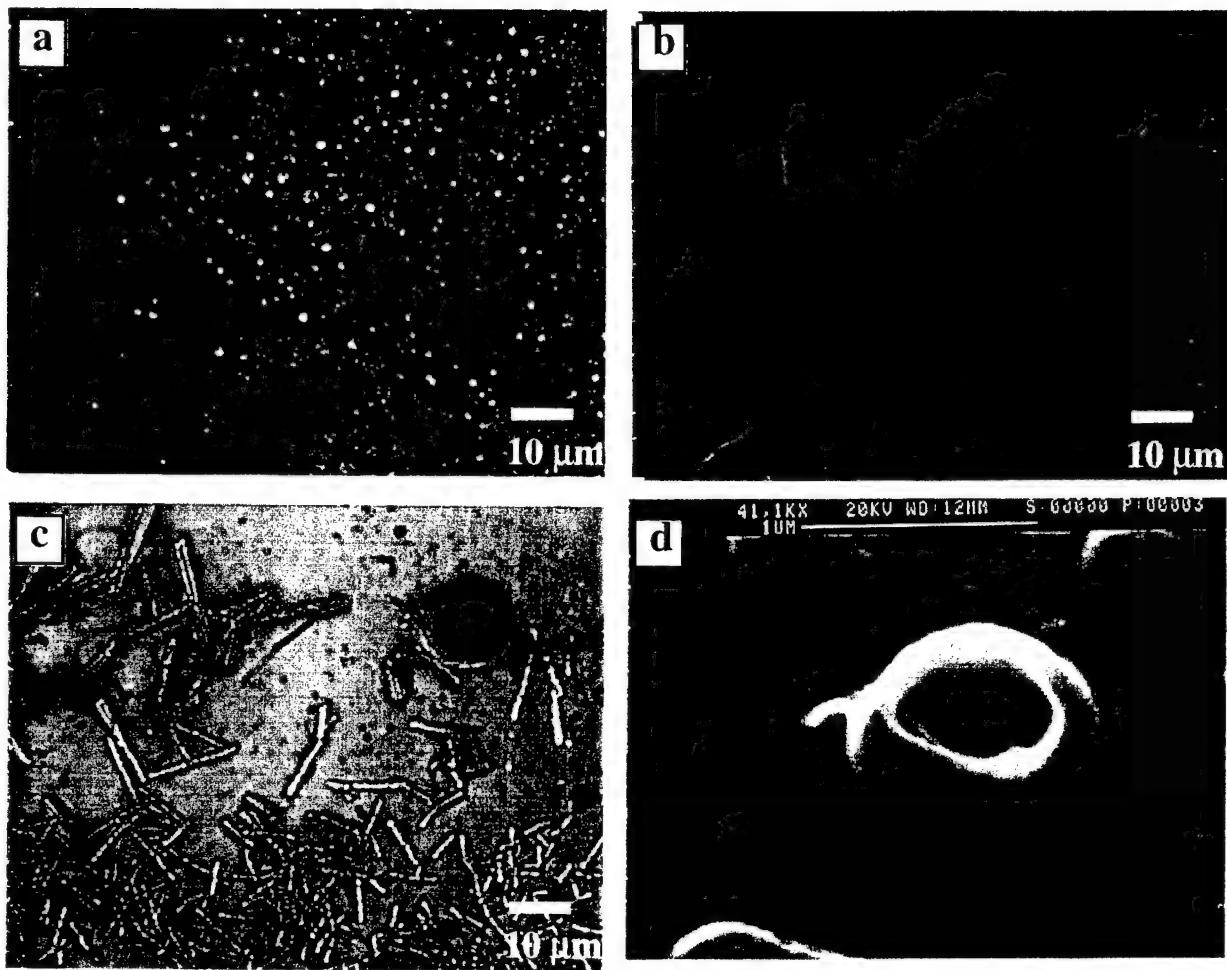
Fig. 3. (A) Photoluminescence (PL) emission and excitation (PLE) spectra and (B) PL decay dynamics of spherical, lamellar, and cylindrical aggregates of PPQ₅₀-PS₃₀₀. PL emission spectra are for 380-nm excitation, and PLE spectra were obtained by monitoring the emission peaks. PL decay data are for 380-nm laser excitation in time-correlated single-photon counting experiments (15).

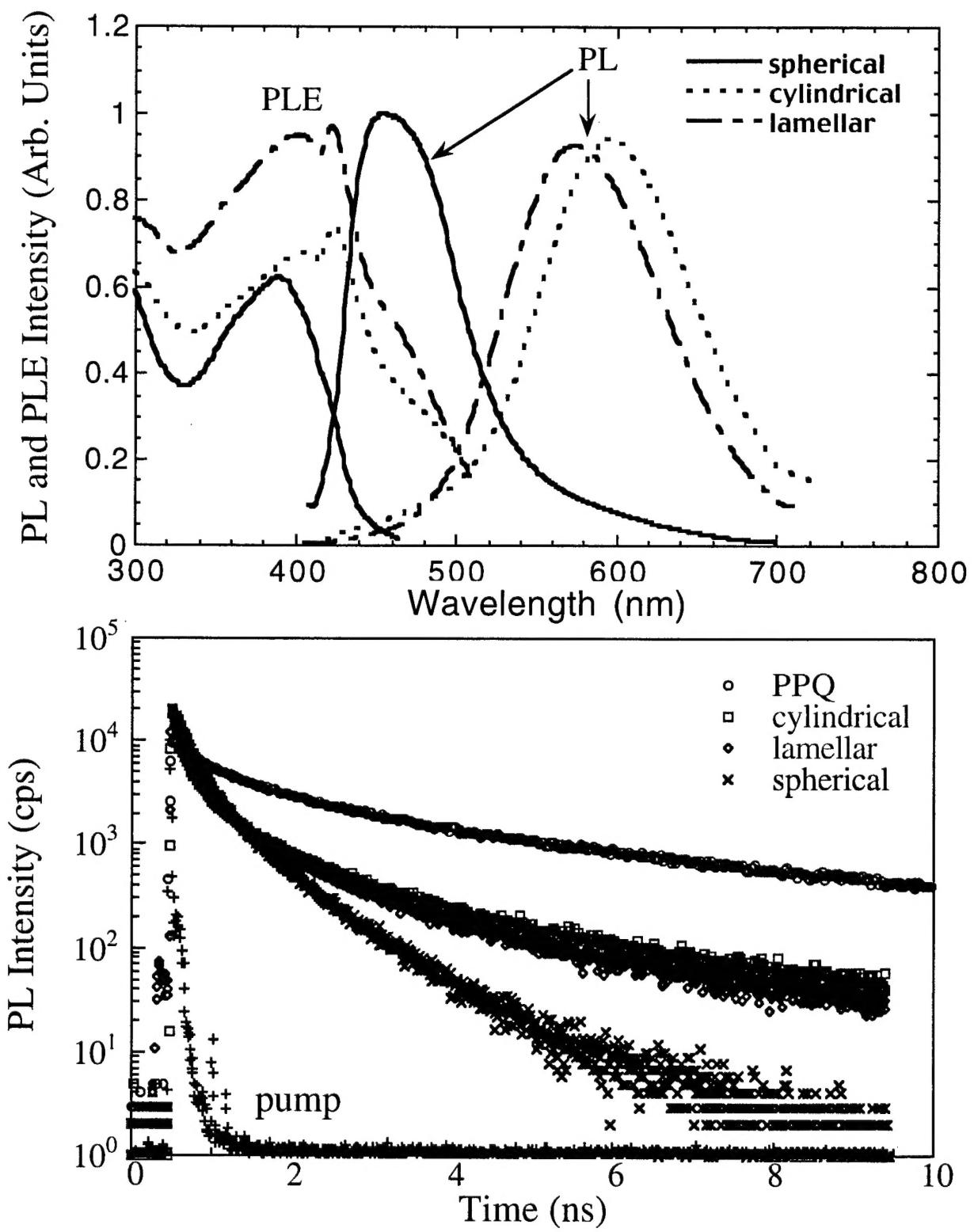
Fig. 4. Fluorescence photomicrographs of PPQ₅₀-PS₃₀₀ aggregates shown in Fig. 2. (A) Spherical, (B) lamellar, (C) cylindrical, and (D) vesicular aggregates.

Fig. 5. Optical micrographs of aggregates of PPQ₅₀-PS₃₀₀ containing 5 wt % solubilized C₆₀: sample from 1:1 TFA:DCM under (A) bright field ; and sample from 1:1 TFA:toluene under (B) cross-polarizers. (C) Schematic illustration of the cross-section of a spherical block copolymer aggregate with encapsulated fullerene-C₆₀.

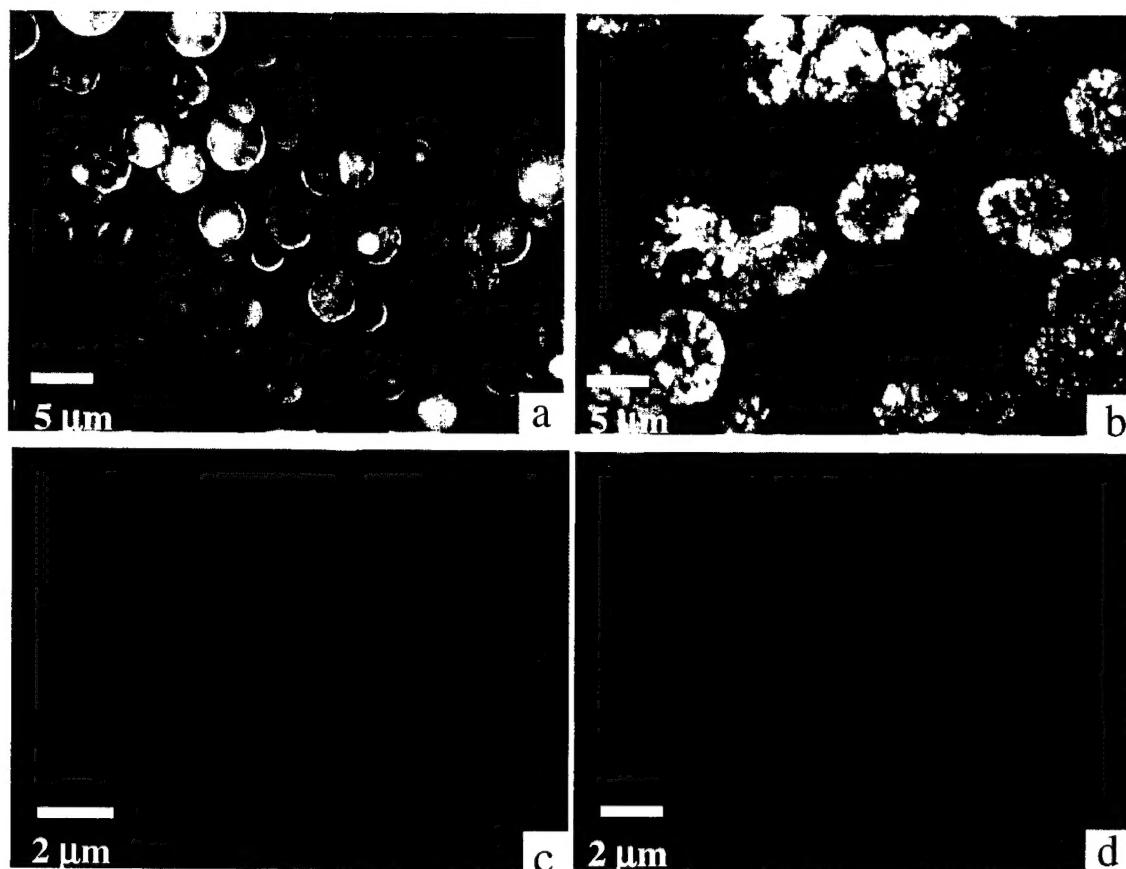
Fig. 1







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Fig. 4



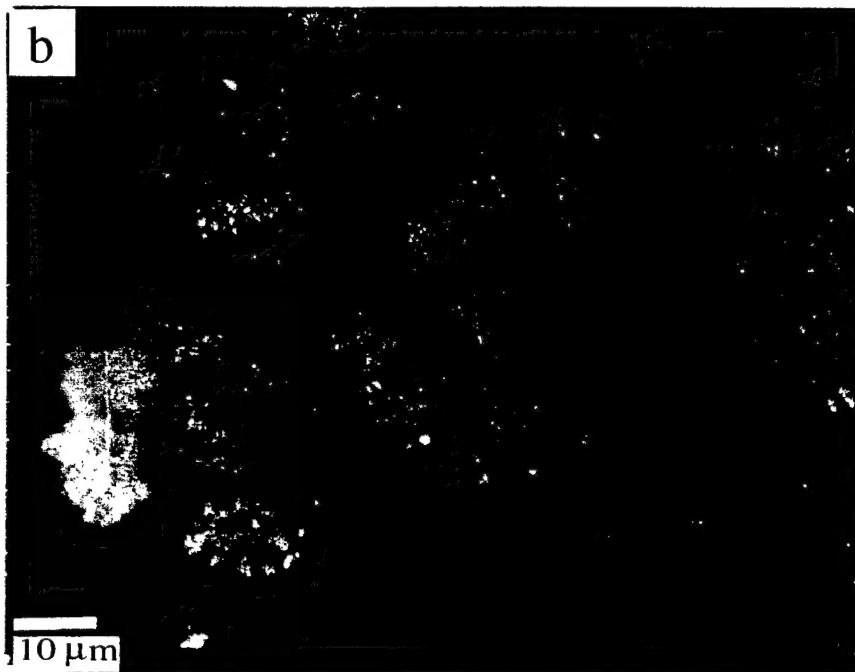
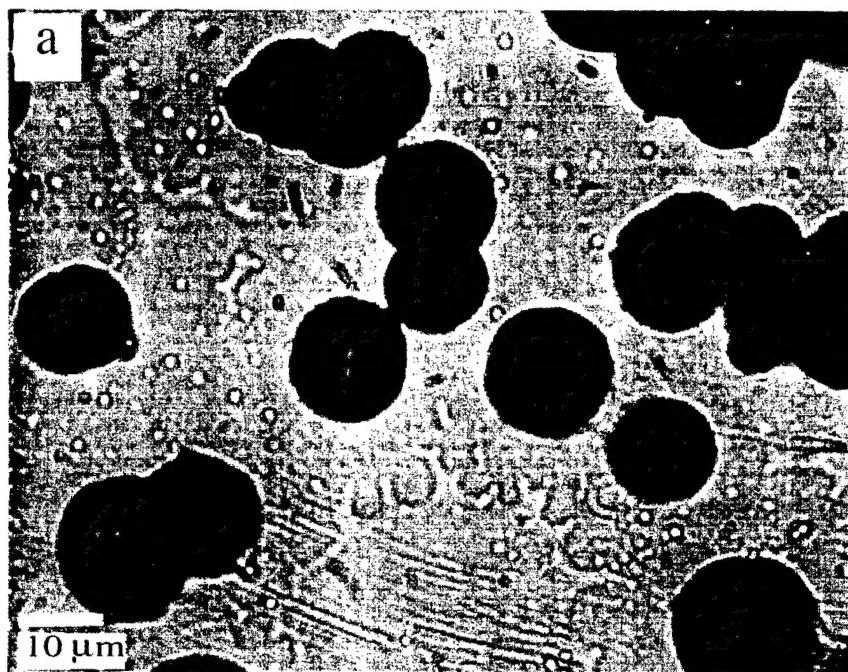


Fig. 5c

